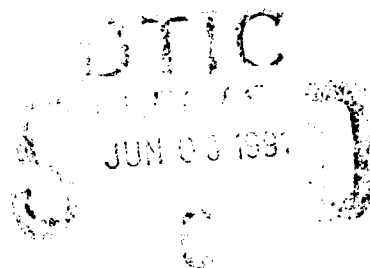


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TITLE OF CONTRACT: Characterization of the Interfacial Regions of Heterogeneous Blends of Immiscible Polymers by Dynamic Nuclear Polarization <sup>13</sup>C NMR

PRINCIPAL INVESTIGATOR: Jacob Schaefer

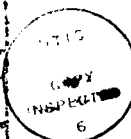
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ATTENTION PROGRAM OFFICERS: This project is continuing under contract number N00014-90-J-4118. The format of this report is in response to instructions by program director, Dr. Kenneth J. Wynne.

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CHARACTERIZATION OF THE INTERFACIAL REGIONS  
OF HETEROGENEOUS BLENDS OF IMMISCIBLE POLYMERS BY  
DYNAMIC NUCLEAR POLARIZATION CARBON-13 NUCLEAR MAGNETIC RESONANCE

PROJECT SUMMARY

By doping one component of an immiscible blend of two polymers with a stable free radical, we can generate a dynamic nuclear polarization (DNP) enhanced  $^{13}\text{C}$  NMR signal from chains of the undoped component which are within 100 Å of the interface. DNP-enhanced NMR relaxation experiments performed on polycarbonate/free-radical-doped-polystyrene blends show that polycarbonate chains in the vicinity of the polystyrene interface are more densely packed than are polycarbonate chains in the bulk state. We propose to perform DNP-selected, NMR relaxation experiments on a variety of polycarbonate-polystyrene blends with known thermal histories and solvent exposure. The results of these experiments could lead to a connection between microscopic interface properties and macroscopic mechanical properties. Making this connection will be aided by theoretical modeling of the interface region between glassy polymers using a generalized Langevin simulation method. We also propose to select chains at the interface of a heterogeneous blend by rotor-synchronized flipping of electron spins in the doped phase. No polarization transfer is involved in this combined pulsed ESR/NMR experiment which should be more generally applicable than the DNP selection technique. Carbon-13 observed, rotational-echo double-resonance (REDOR)  $^1\text{H}/^{13}\text{C}/^{19}\text{F}$  NMR experiments are also planned. In these experiments, instead of doping one component of a blend with stable free radicals, we propose to dope with  $^{19}\text{F}$  stable-isotope labels. Dipolar dephasing of carbon magnetization in the undoped phase by fluorines in the doped phase will select chains within 10 Å of the interface.

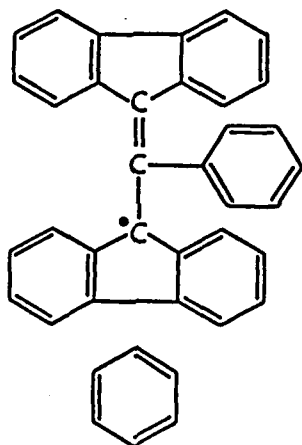
## INTRODUCTION

This report describes work done under ONR grant N00014-88-K-0183, "Characterization of the Interfacial Regions of Heterogeneous Blends of Immiscible Polymers by Dynamic Nuclear Polarization  $^{13}\text{C}$  NMR." This work involves the incorporation of stable free radicals into just one of the components of a blend of two incompatible polymers. The free-radical is pumped by microwave irradiation and the resulting polarization is transferred first to protons, and then from protons to carbons, where it is detected under high-resolution, magic-angle spinning conditions. Any carbon magnetization arising from chains in the undoped phase, which can be traced back to the pumping of the free radical, is an interface signal. The chains responsible for this signal can be no more than 100 Å or so from the free-radical source of magnetization. This specificity can therefore be used to examine the structure and dynamics of polymer-blend interfaces directly and unambiguously. We believe that microscopic interface properties determine the macroscopic mechanical properties of blends and composites.

## DESCRIPTION OF WORK

1. *Detection of an Interface Signal in Polystyrene/Polycarbonate Blends:* Bisdiphenylene phenylallyl (BDPA) free radical (Figure 1) forms a solid solution

Figure 1. Structure of  $\alpha,\gamma$ -bisdiphenylene- $\beta$ -phenyl allyl (BDPA) free-radical complex with benzene.



[Goldsborough et al, 1960] with polystyrene (PS) when precipitated from a common solvent. Microwave irradiation at the sum or difference of the Larmor frequencies of the electron and proton generates a net enhancement of the proton polarization [Goldman, 1970] in a solid solution of BDPA in PS. This phenomenon is the so-called "solide" dynamic nuclear polarization (DNP) effect (Figure 2). Sizeable enhancements are achieved even with modest microwave power by the solide effect (microwave transitions do not have to be saturated) if the ESR spectrum of the free radical is simple (no hyperfine splittings) and the  $T_1$  of the protons is long (no polarization leakage). Both of these conditions are satisfied [Wind et al, 1985] for BDPA in polystyrene, designated PS(\*). After a transfer of magnetization from protons to carbons, the DNP cross-polarization, magic-angle spinning (CPMAS)  $^{13}\text{C}$  NMR spectrum of PS(\*) is enhanced by a factor of 20 relative to a standard CPMAS spectrum (Figure 3).

One of our primary goals during the last three years has been to generate a  $^{13}\text{C}$  signal from polycarbonate (PC) chains at the interface of blends with doped PS. We designate such blends, PC/PS(\*). We anticipated that bulk PS signals would be strong compared to

Figure 2. Dynamic nuclear polarization by the solid effect. A single electron (big arrow) is dipolar coupled to many isolated nuclei (small arrows). Irradiation at the sum of the nuclear (I) and electron (S) Larmor frequencies induces forbidden double-quantum transitions. The electron spin-lattice relaxation time ( $T_S$ ) is short while the nuclear spin-lattice relaxation times are long. Thus, a single electron can polarize many nuclei under microwave pumping.

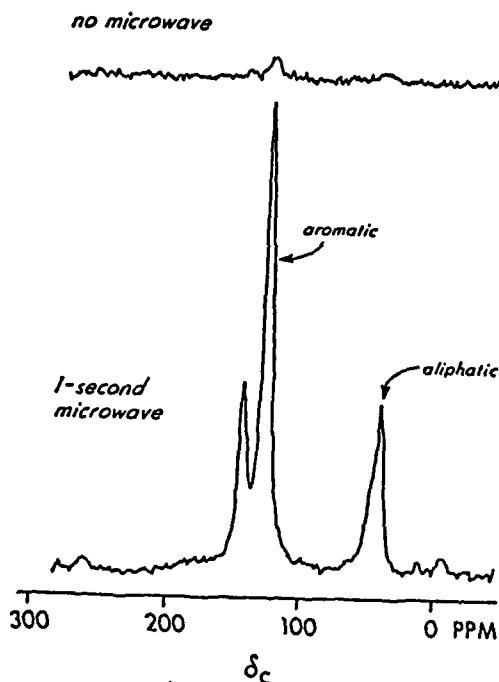
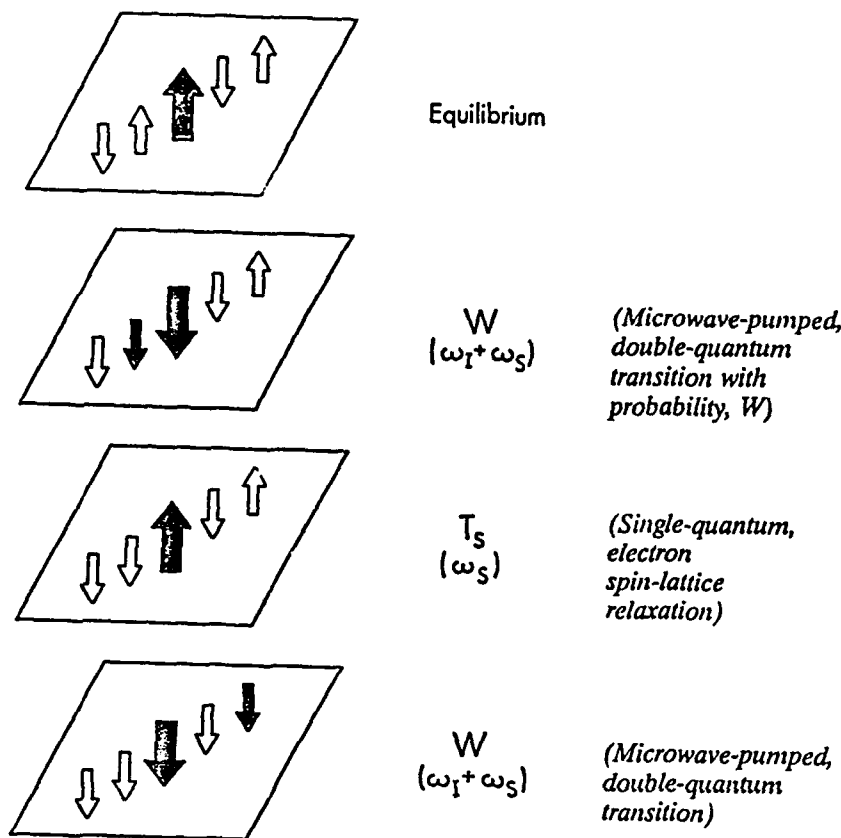


Figure 3. 15.1-MHz CPMAS  $^{13}\text{C}$  NMR spectra of BDPA-doped polystyrene with (bottom) and without (top) 1-sec microwave irradiation.

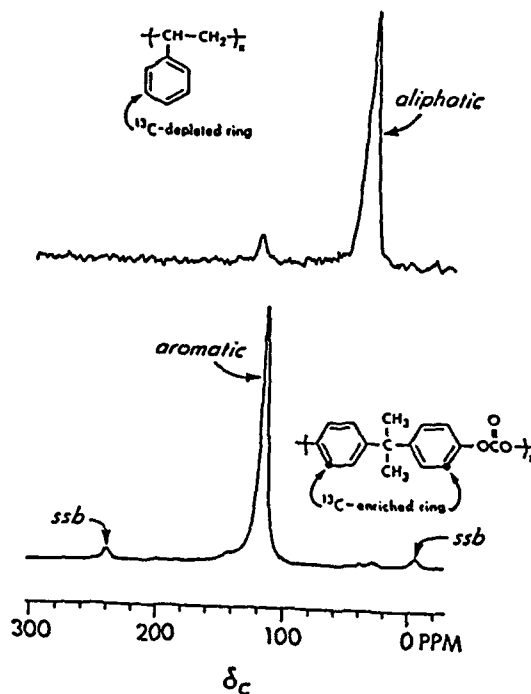


Figure 4. 15.1-MHz CPMAS  $^{13}\text{C}$  NMR spectra of a  $^{12}\text{C}$ -enriched polystyrene (top) and a  $^{13}\text{C}$ -enriched polycarbonate (bottom). Spinning sidebands are designated "ssb".

interface PC signals, and so decided to make blends from  $^{13}\text{C}$ -depleted polystyrene and  $^{13}\text{C}$ -enriched polycarbonate (Figure 4). The bulk PS signal would therefore not overwhelm the interface PC signal.

The blends were formed by serial casting of two films (Figure 5). First, PC was cast

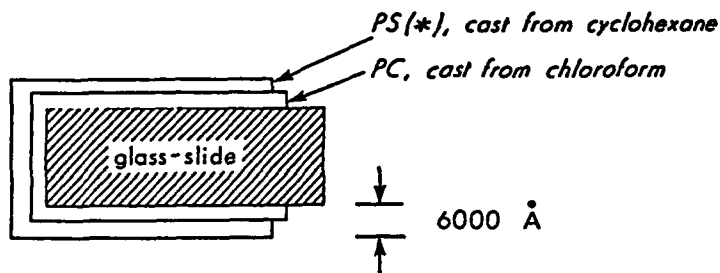


Figure 5. Preparation of a thin-film blend of polystyrene and polycarbonate by double casting.

on a microscope slide from chloroform and dried in a vacuum oven at 50° C. A second film was cast on top of the first from a cyclohexane solution of PS and BDPA at 38° C. Cyclohexane is a non-solvent for PC. After drying, the most uniform part of the sandwich film was scraped from the center section of the microscope-slide casting using a razor blade. About 1.5 mg of film was recovered from each slide; 150 mg of film were pressed at 500 psi and room temperature to make a pellet for the magic-angle rotor.

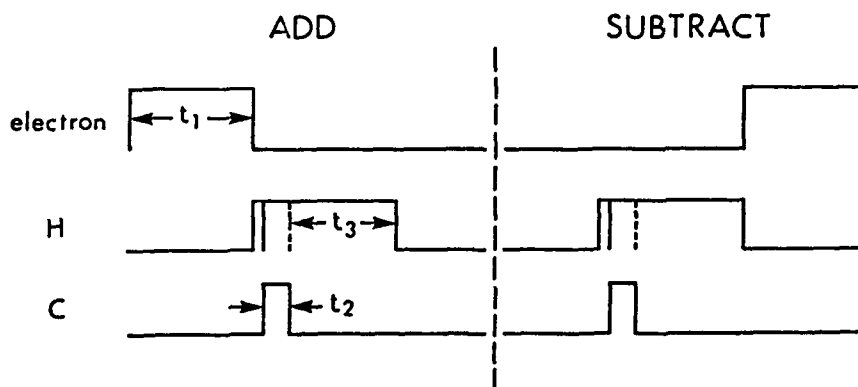


Figure 6. Pulse sequence for DNP-enhanced difference CPMAS  $^{13}\text{C}$  NMR. Microwave pumping occurs during  $t_1$ , cross polarization during  $t_2$ , and  $^{13}\text{C}$  acquisition with  $^1\text{H}$  dipolar decoupling during  $t_3$ .

The scheme to generate an interfacial PC signal uses an add-subtract pulse sequence (Figure 6). Normal CPMAS signals in PC homopolymer are cancelled exactly by this scheme (Figure 7). A DNP enhancement is, however, observed for both PC and PS components of a PC/PS(\*) blend (Figure 8). The natural-abundance aliphatic-carbon signal of bulk PS ( $\delta_c$  45) is about 5 times larger than the  $^{13}\text{C}$ -enriched aromatic-carbon signal of interface PC ( $\delta_c$  120). With an expanded vertical scale, a minor contribution can also be observed from the  $^{13}\text{C}$ -depleted PS aromatic rings ( $\delta_c$  125, Figure 9). In PC/PS(\*) blends, only  $^{13}\text{C}$  signals whose origin can be traced back to the electron survive. These include bulk and interfacial PS, and interfacial PC signals. Bulk PC signals are not present because free radicals are excluded from the PC phase. The absence of BDPA free radicals in the

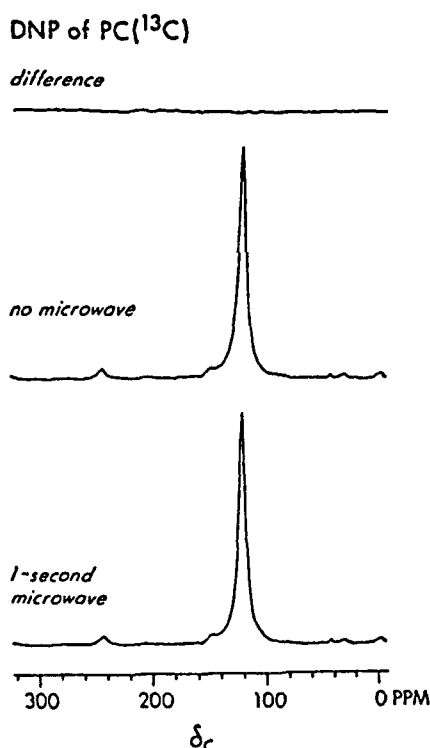


Figure 7. 15.1-MHz CPMAS  $^{13}\text{C}$  NMR of  $^{13}\text{C}$ -enriched polycarbonate with (bottom) and without (middle) 1-second microwave irradiation. The difference between the two is the null spectrum shown at the top of the figure.

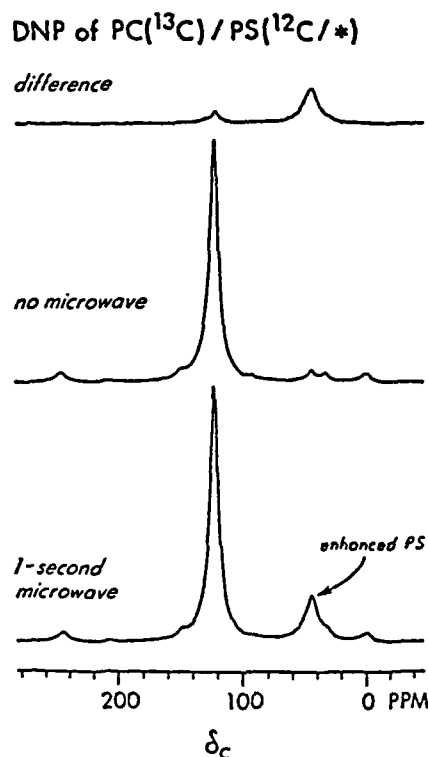


Figure 8. 15.1-MHz CPMAS  $^{13}\text{C}$  NMR of a thin-film blend of  $^{13}\text{C}$ -enriched polycarbonate and BDPA-doped  $^{12}\text{C}$ -enriched polystyrene with (bottom) and without (middle) microwave irradiation. The difference spectrum (top) has a polycarbonate contribution ( $\delta_c$  120) arising from chains at the interface.

bulk PC phase was confirmed by a casting of BDPA from cyclohexane at 38° C on a PC film. There was no penetration of the PC film and hence no contact with BDPA on a molecular level. After drying, BDPA formed crystals on the film surface. Because BDPA was not molecularly dispersed, no DNP enhancement is observed (Figure 10, top).

DNP Difference of PC( $^{13}\text{C}$ ) / PS( $^{12}\text{C}$  / \*)  
1-sec microwave irradiation

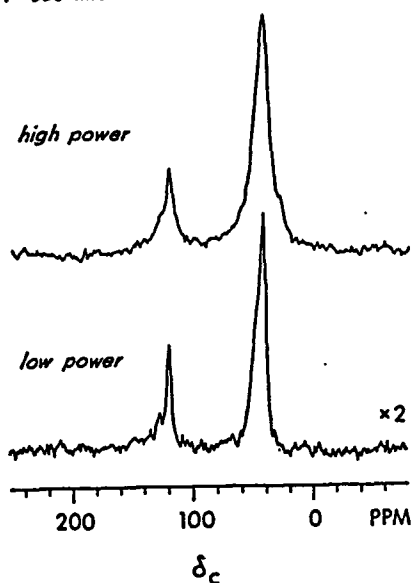


Figure 9. 15.1-MHz CPMAS  $^{13}\text{C}$  NMR DNP difference spectra of the sample of Figure 8. Increasing the microwave power increases the difference intensity but broadens the lines.

DNP of PC( $^{13}\text{C}$ ) / \*

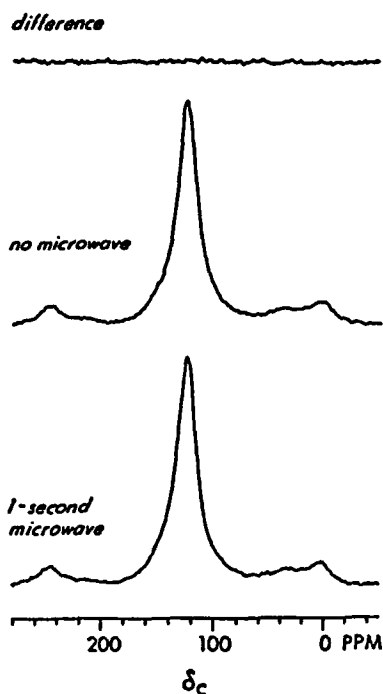


Figure 10. 15.1-MHz CPMAS  $^{13}\text{C}$  NMR spectra of a  $^{13}\text{C}$ -enriched polycarbonate film dipped in a cyclohexane solution of BDPA and then dried. The BDPA has crystallized on the surface of the film. The linewidth is due to bulk susceptibility broadening. The spectra were obtained with (bottom) and without (middle) 1-second microwave irradiation.

**2. Mechanism of Polarization Transfer Across the Interface:** Two possibilities exist to account for the origin of the interfacial PC  $^{13}\text{C}$  NMR signal. The first possibility is that dipolar contact between protons in PS and PC carries polarization across the interface by  $^1\text{H}$ - $^1\text{H}$  spin diffusion. The second possibility is that the solide effect works directly between the unpaired electrons of free radicals in the PS phase near the interface and protons in the PC phase on the other side of the interface (Figure 11).

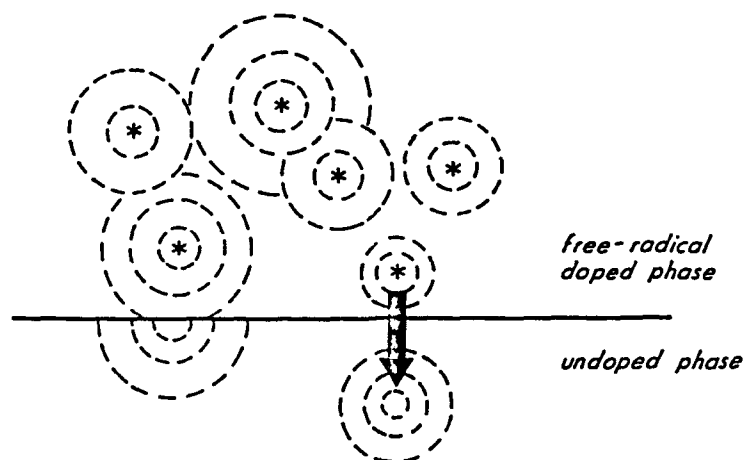


Figure 11. Polarization transfer from electrons (stars) to protons in the undoped phase of a two-phase heterogeneous blend can occur directly or indirectly, the latter by  $^1\text{H}$ - $^1\text{H}$  spin diffusion.

To establish the mechanism, we made BDPA-doped films from perdeuterated polystyrene. The DNP enhancement for the residual protons in these films was the same as for PS(\*) films, although the time required to reach full enhancement was slightly longer (Figure 12). This means that in bulk PS( $^2\text{D}/*$ ), and probably even in the bulk phase of fully protonated PS(\*), the dominant long-range transfer mechanism is direct coupling to the electron. Spin diffusion only homogenizes the distribution of polarization locally, moving it away from those protons most strongly coupled to electrons.

A PC blend made with the BDPA-doped perdeuterated PS resulted in DNP-enhanced PC interface signals of equal integrated intensity relative to that of the all-protonated film (Figure 13, top and bottom). The PC interface signal is broadened slightly for this sample because of a bulk susceptibility effect that we attribute to minor aggregation of BDPA. (The unenhanced, standard CPMAS bulk PC signal was also broadened). Magic-angle spinning  $^1\text{H}$  NMR shows that the  $^1\text{H}$ - $^1\text{H}$  dipolar coupling in perdeuterated PS has been reduced by a factor of 200 relative to fully protonated PS. Thus, we conclude that the PC interface signal is generated by a direct transfer from electrons in the PS phase across the interface to protons in the PC phase. This magnetization is subsequently homogenized and distributed locally in the PC phase by

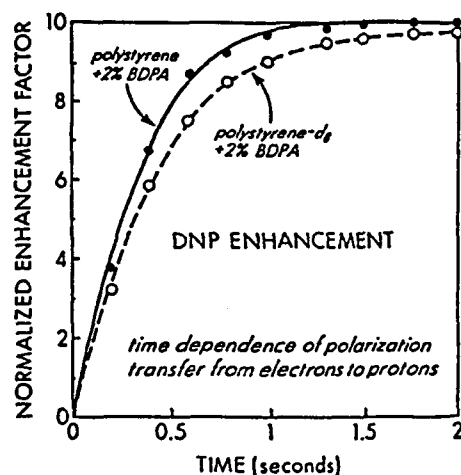


Figure 12. DNP enhancement of the  $^1\text{H}$  NMR signal intensity as a function of the microwave irradiation time for BDPA-doped polystyrene and 98% perdeuterated polystyrene.

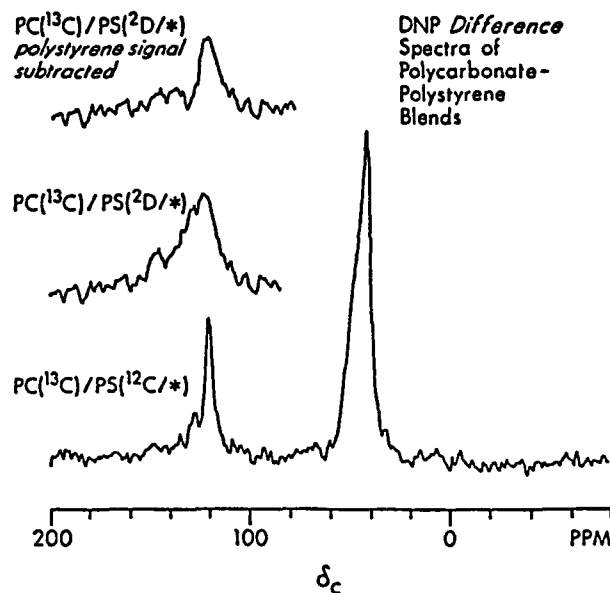


Figure 13. DNP difference  $^{13}\text{C}$  NMR spectra of polycarbonate blends with BDPA-doped polystyrene. The bottom spectrum also appears in Figure 10. The spectra in the inserts arise from natural-abundance carbons coupled to the residual protons in a perdeuterated polystyrene.

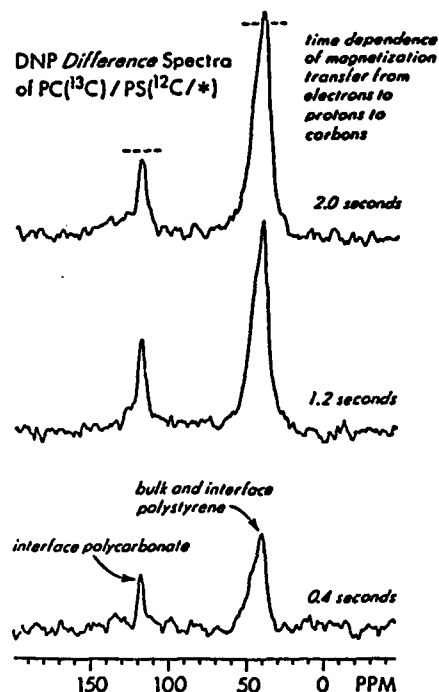
$^1\text{H}$ - $^1\text{H}$  spin diffusion.

Some of the interfacial PC signal arises from chains relatively distant from electrons (more than 50 Å). Spin diffusion carries polarization generated by microwave pumping farther and farther away from the interface to PC chains not coupled effectively to the electron centers. The total interface signal therefore depends on the  $^1\text{H}$  spin-



lattice lifetime of polarization in the interfacial and near-interfacial PC regions. We have described the time dependence of magnetization transfer from electrons to protons to carbons (Figure 14) using a one-dimensional Fickian diffusion model [Crank, 1956]

Figure 14. DNP difference  $^{13}\text{C}$  NMR spectra of a  $^{13}\text{C}$ -enriched polycarbonate blend with BDPA-doped,  $^{12}\text{C}$ -enriched polystyrene as a function of the microwave irradiation time. The DNP enhancement for PC reaches a maximum after irradiation for about 1.2 seconds and then decreases because of spin-lattice relaxation. The dotted lines indicate signal levels for 1.2-seconds irradiation.



with interfacial-PC proton spin-lattice relaxation. The model predicts a downturn of the magnetization versus microwave irradiation time for interface PC but not for bulk PS (Figure 15). In PS(\*), all chains are sufficiently near an electron center that relaxation is not important.

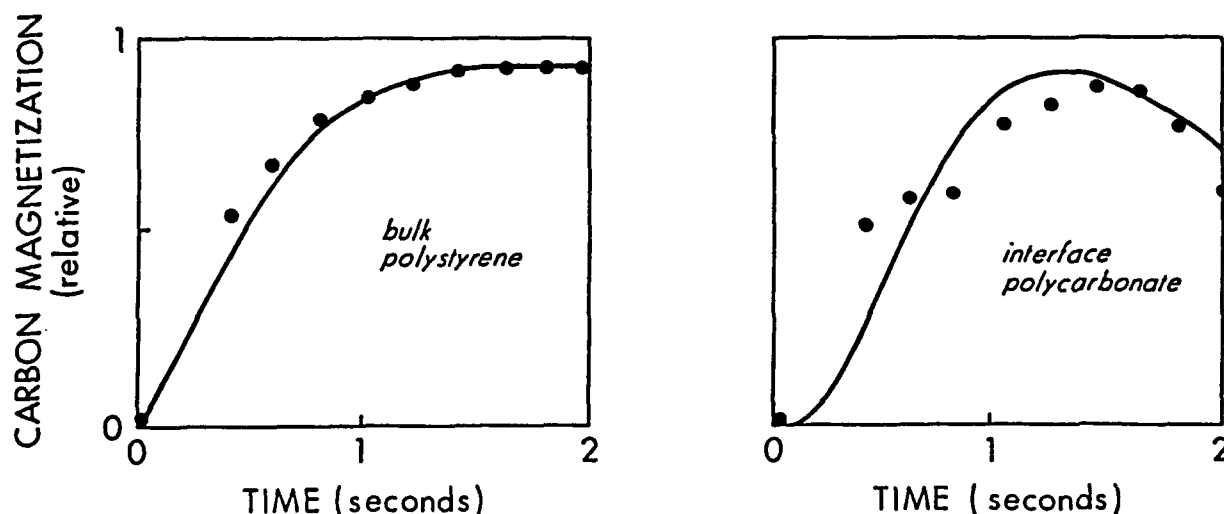


Figure 15. Relative DNP difference  $^{13}\text{C}$  NMR signals intensities as a function of microwave irradiation time for bulk polystyrene (left) and interface polycarbonate (right) in a heterogeneous blend of  $^{13}\text{C}$ -enriched polycarbonate with BDPA-doped  $^{12}\text{C}$ -polystyrene. Circles are experimental points and solid curves were calculated from a Fickian diffusion model (with spin-lattice relaxation) of spin diffusion.

3. **Molecular Dynamics of Interfacial PC Chains:** Having generated and confirmed a  $^{13}\text{C}$  NMR signal arising exclusively from PC chains near the PC/PS interface, we can now perform NMR relaxation experiments to characterize the microscopic dynamics of these chains. A difference pulse sequence is used which is similar to that of Figure 6, but which includes a period for carbon dephasing under the influence of dipolar coupling to protons [Munowitz and Griffin, 1982; Schaefer et al, 1984] isolated from one another by multiple-pulse  $^1\text{H}$ - $^1\text{H}$  decoupling (Figure 16).

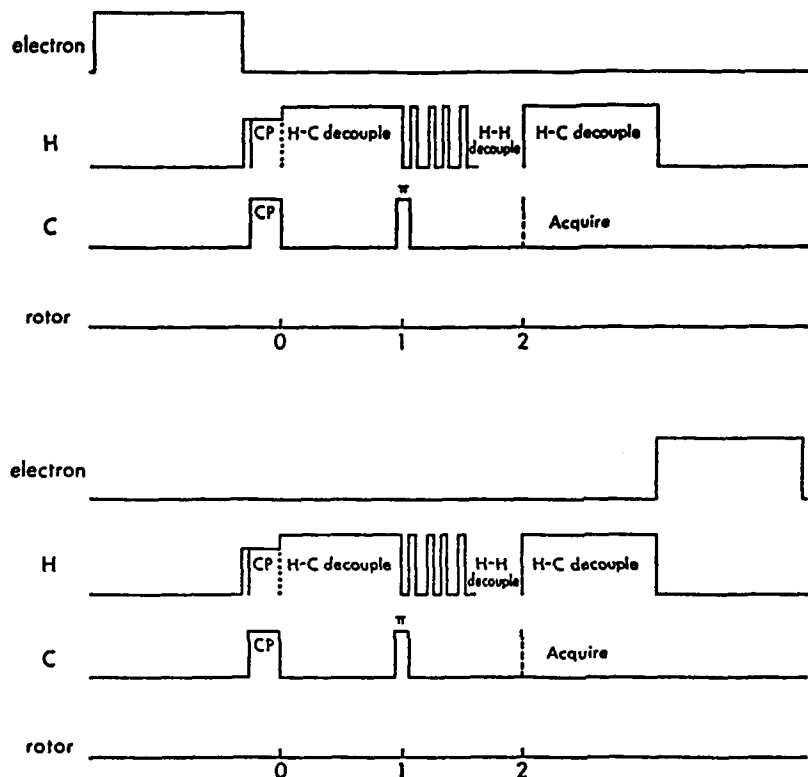
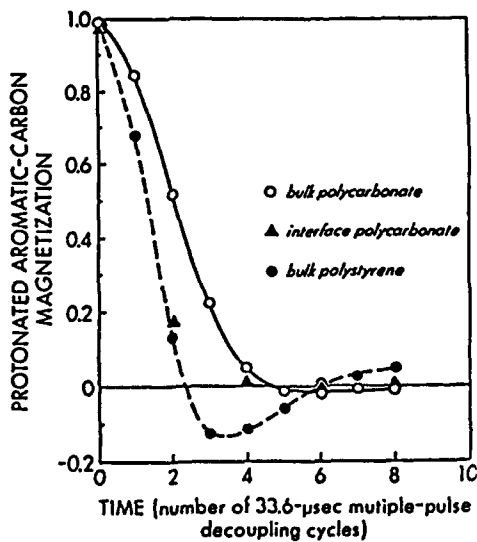


Figure 16. Pulse sequence for dipolar, rotational spin-echo  $^{13}\text{C}$  NMR of carbons selected by DNP differencing. The acquisition alternates between addition and subtraction (top and bottom, respectively). Only signals that can be traced back to the microwave pumping accumulate.

Figure 17. Dephasing of the  $^{13}\text{C}$  NMR magnetization of bulk polycarbonate, bulk polystyrene, and interface polycarbonate due to C-H dipolar coupling with  $^1\text{H}$ - $^1\text{H}$  dipolar coupling removed by multiple-pulse proton decoupling. The faster the decay, the more restricted the molecular motion.



Faster dephasing (decay) is observed for interface PC than for bulk PC (Figure 17). The faster dipolar dephasing means a stronger  $^1\text{H}$ - $^{13}\text{C}$  dipolar coupling and hence less motional averaging [Schaefer et al, 1984]. We believe that chains at the interface are more densely packed than in the bulk. Monte-Carlo, off-lattice, computer simulations [Kumar et al, 1989] have shown that near the interface, enthalpic repulsions are more important

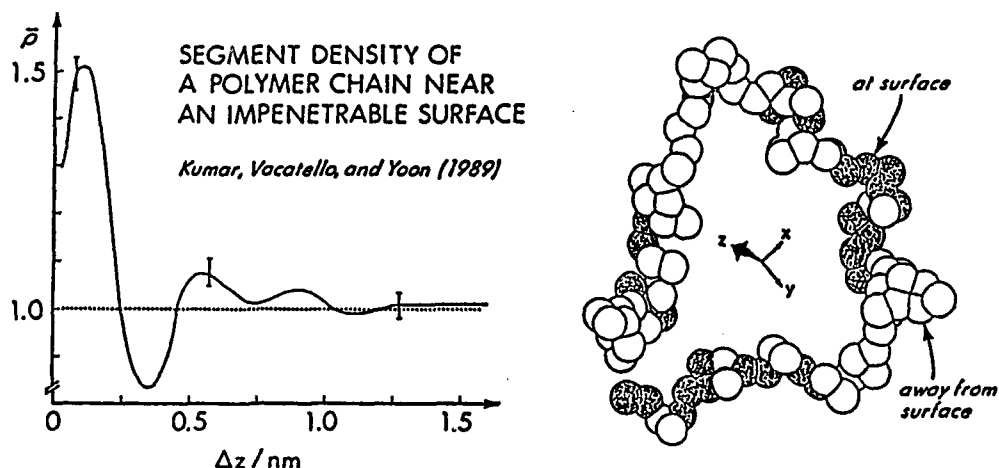


Figure 18. Left: calculated segment density of a polyethylene chain as a function of the distance from an impenetrable wall, normalized with respect to the density of liquid tridecane at room temperature. Right: Three dimensional structure of a polyethylene chain near an impenetrable surface. The wall lies beneath the chain; all atoms within 5 Å of the wall are denoted by filled symbols. (After Kumar, Vacatello, and Yoon, 1989).

to packing than entropic effects (Figure 18). The rings of bulk PC main chains undergo  $180^\circ$  flips about their  $\text{C}_2$  axes. Flips are controlled by volume (bulk) and shape (shear) reorganizations of the lattice [Schaefer, et al, 1985]. The tighter packing of interface PC chains means that local density fluctuations are insufficient to permit ring flips. This loss of motion leads to faster  $^1\text{H}$ - $^{13}\text{C}$  dipolar dephasing. In general, PS rings are also not capable of such motions, consistent with the observed fast dephasing for bulk PS (Figure 17).

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